Atomic-Scale Optical Spectroscopy

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2016 Gerhard Ertl Young Investigator Award
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Optical imaging and spectroscopy at atomic resolution is an overarching goal in modern nanoscale science and technology, allowing us to directly access atomic-scale structures and dynamics in real space and real time. Atomic-scale crystal imperfections, defects and inhomogeneities indeed play a crucial role in physicochemical properties and functions of solid catalysts and semiconductor optoelectronic devices. We have challenged to attain atomic-scale optical spectroscopy by combining advanced low-temperature scanning tunneling microscopy, laser spectroscopy and nanoplasmonics.

Electromagnetic fields can be confined to nanoscale through excitation of localized surface plasmon resonances of metallic nanostructures. Plasmonics is a mature research field, enabling precise control of nanoscale light. Accordingly, nanoscale optical imaging and spectroscopy well below the diffraction limit has become a more routine technique. However, the typical spatial resolution remains a few tens of nanometers, which is still far from the atomistic length scale. More recently, state-of-the-art experiments and theories demonstrated that atomic-scale confinement of electromagnetic fields occurs at atomistic asperities existing on metallic nanostructures. However, it is an outstanding challenge to precisely manipulate atomically confined light. We have developed advanced experimental techniques to manipulate extremely confined, strong plasmonic fields in scanning tunneling microscope junctions and implemented ultrasensitive and ultrahigh resolution optical spectroscopy. We also investigate intriguing atomic-scale strong light–matter interactions in an atomically well-defined environment.

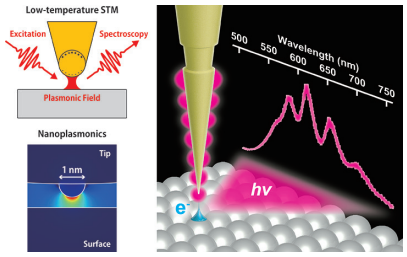

Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- H. Böckmann, S. Liu *et al.*, "Near-Field Manipulation in a Scanning Tunneling Microscope Junction with Plasmonic Fabry-Pérot Tips," *Nano Lett.* **19**, 3597–3602 (2019).
- S. Liu *et al.*, "Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation," *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, "Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface," *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, "Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction," *ACS Photonics* **8**, 2610–2617 (2021).
- B. Cirera *et al.*, "Charge Transfer-Mediated Dramatic Enhancement of Raman Scattering upon Molecular Point Contact Formation," *Nano Lett.* **22**, 2170–2176 (2022).
- S. Liu *et al.*, "Nanoscale Heating of an Ultrathin Oxide Film Studied by Tip-Enhanced Raman Spectroscopy," *Phys. Rev. Lett.* **128**, 206803 (2022).

1. Inelastic Light Scattering by a Plasmonic Nanogap

Light scattering from plasmonic nanojunctions is routinely used to assess their optical properties. However, the microscopic mechanism remains imperfectly understood, and an accurate description requires the experiment in a well-defined environment with a highly precise control of the nanojunction. We investigated inelastic light scattering (ILS) in a plasmonic STM junction at cryogenic temperature and found that a broad continuum occurs in the anti-Stokes regime when the bias voltage is applied (Figure 2).[1] The underlying mechanism was examined by recording the ILS spectra concurrently with STM luminescence. We proposed that electronic Raman scattering is dominant when the excitation wavelength matches the gap-mode plasmon, whereas photoluminescence mainly contributes under off-resonance conditions. The results provide an in-depth understanding of ILS by electrically biased plasmonic nanojunctions and demonstrate nonthermal origin of the anti-Stokes scattering.

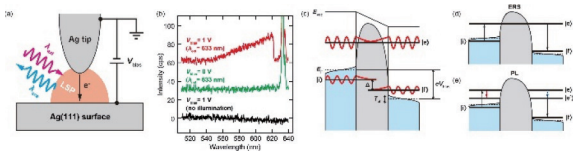

Figure 2. (a) Schematic of the experiment. (b) ILS spectra in the anti-Stokes regime measured for the Ag tip–vacuum–Ag(111) junction at a different bias voltage and in the presence/absence of the illumination. (c–e) Anti-Stokes scattering mechanism in an electrically-biased STM junction. (d) Electronic Raman scattering. (e) Photoluminescence.

2. Atomic-Point Contact Raman Spectroscopy

Tip-enhanced Raman spectroscopy (TERS) is a powerful tool for ultrasensitive chemical analysis at surfaces. Although the enhancement mechanism underlying TERS has been intensively studied, it remains to be elucidated, particularly in sub-nanometer plasmonic gaps. We investigated TERS at atomic-point contacts (APCs) in plasmonic STM junctions and found that large enhancement can be obtained when APCs are formed. Figure 3 shows an example of APC-TERS for an ultrathin ZnO film epitaxially grown on the Ag(111) surface.[2] The TERS spectra are recorded as a function of the tip–surface distance including two distinct regimes, namely the tunneling and APC regimes. The remarkable enhancement can be observed at the distance of the APC formation. We suggest that the enhancement is explained by chemical effects resulting from hybridization between the tip apex and surface atoms of the ZnO film.

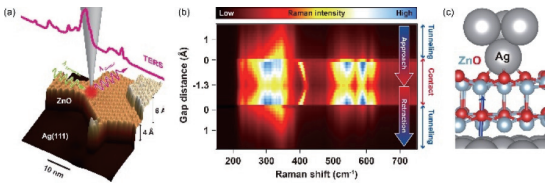

Figure 3. (a) Schematic of the experiment. (b) Waterfall plot of the gap-distance-dependent TER spectra recorded over 2-ML ZnO. The tip approaches and retracts toward and backward from the ZnO from the tunneling to the APC regime. (c) Structure at the APC determined by the DFT calculation.

3. Nanoscale Heating of an Ultrathin Oxide Film

Heating is one of the most basic physical processes. Rapid advances of nanofabrication techniques raise a fundamental issue regarding thermal management at nanoscale. TERS thermometry provides a unique opportunity to study local heating. We investigated the nanoscale heating mechanism of an ultrathin ZnO film using TERS (Figure 4).[3] The exceptional sensitivity of TERS allowed to observe Stokes and anti-Stokes scattering of the ZnO film and to perform nanoscale thermometry. It was revealed that the local heating originates mainly from inelastic electron tunneling through the electronic resonance when the bias voltage exceeds the conduction band edge of the 2-monolayer (ML) ZnO. When the bias voltage is lower than the conduction band edge, the local heating arises from two different contributions, namely direct optical excitation between the interface state and the conduction band of 2-ML ZnO or injection of photoexcited electrons from an Ag tip into the conduction band. Simultaneous mapping of tip-enhanced Raman spectroscopy and scanning tunneling spectroscopy for 2-ML ZnO including an atomic-scale defect demonstrates visualizing a correlation between the heating efficiency and the local density of states, which further allows us to analyze the local electron-phonon coupling strength with ~2 nm spatial resolution.

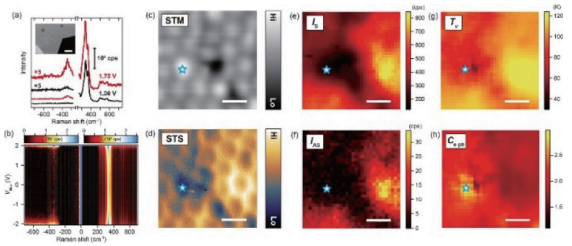

Figure 4. (a) TERS spectra of 2-monolayer ZnO/Ag(111) including the Stokes and anti-Stokes regimes. (b) Waterfall TERS plot as a function of the applied bias voltage. (c) and (d) STS image of 2-monolayer ZnO film including an atomic-scale defect and the corresponding STS mapping. (e–g) Mapping of the Stokes and anti-Stokes intensity and the effective temperature recorded in the same area with (c–d). (f) Mapping of the relative electron–phonon coupling strength.

References

1) S. Liu *et al.*, *ACS Photonics* **8**, 2610–2617 (2021).
2) S. Liu *et al.*, *Nano Lett.* **20**, 5879–5884 (2020).
3) S. Liu *et al.*, *Phys. Rev. Lett.* **128**, 206803 (2022).